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THE BLUE SHIFTS OF THE C-H AND N-H BONDS IN THE COMPLEXES OF CHX_3 (X = F, Cl, Br) AND HNO: A THEORETICAL STUDY

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ABSTRACT

All calculations were performed at the high level of theory (MP2/6-311++G(d,p)). Five separate minima were identified on the potential energy surface of each complex pairing CH_3X with HNO. In general, strength of complexes increases in going from F to Cl to Br, which is consistent with respective decrease of deprotonation enthalpy of the C-H bond respectively. All the C-H and N-H bonds are shortened upon complexation, corresponding to increase in their stretching frequencies. It is interesting that blue shift is observed in the N-H bonds; such a contraction in the N-H covalent bond is extremely rare. Linear correlation between change of stretching frequencies and change of the N-H and C-H bond lengths in all complexes has been reported in equation (1) and (2). Besides, the change of the N-H bond lengths and their stretching frequencies as a function of the change of occupation of σ(N-H) orbitals and that of s-character of N hybrid orbitals were obtained as in expression (3) and (4).*

I - INTRODUCTION

The hydrogen bond A-H...B plays an important role in many chemical, physical and biochemical processes [1, 2]. Recently, a new type of intermolecular bond, commonly designated as a blue-shifting hydrogen bond, continues to receive a good deal of both experimental and theoretical attention. The majority of these blue-shifting hydrogen bonds contains a C-H bond as the proton donor. In general, the N-H bond will shift to the red of stretching frequency because of its more polarization. However, there are some very small numbers of exceptions recently reported for the N-H bond that the blue shift is found in the type of the N-H...O and N-H...X (F, Cl, Br) hydrogen bonds [3 - 5]. Simultaneously, the complexes that combine CHX_3 (X = F, Cl, Br) with HNO are of paramount interest in the field of atmospheric chemistry. In spite of the potential importance of these complexes, there is available in the literature neither theoretical nor experimental information. Our other purposes when considering the interaction between HNO and CHX_3 are to reveal the blue shift of N-H bond in more systems, to provide some interesting data and also to understand the more obvious origin of blue-shifting hydrogen bond.

2. Computational Methods

All calculations of the isolated monomers and their complexes were performed within the second order perturbation method (MP2) in conjunction with the 6-311++G(d,p) basis set using the GAUSSIAN 03 program [6]. The interaction energies were corrected for basis set

superposition errors (BSSE) via the standard counterpoise procedure of Boys and Bernadi [7]. Charges on individual atoms, orbital occupancies and hyperconjugation energies were obtained by the natural bond orbital (NBO) population scheme [8].

III - RESULTS AND DISCUSSION

1. Interaction Energies, Geometries and Stretching Frequencies

The structures of monomers and their complexes were optimized at the high level of theory (MP2/6-311++G(d,p)). The geometries of optimized structures of the complexes were displayed in figure 1. Five minima are located on the potential energy surface of each complex. The interaction energies with ZPE and BSSE corrections were gathered in table 1. The binding energies lie in the ranges of 7 - 11 kJ.mol^{-1} with BSSE correction and 4 - 8 kJ.mol^{-1} with both the ZPE and BSSE corrections. In general, the strength of complexes increases in going from F to Cl to Br, which is in consistent with decreasing of the deprotonation enthalpy of the C-H bond in the isolated monomers with the values of 1577, 1496 and 1463 kJ.mol^{-1}, respectively [9]. There is only an exception that the binding energy in **S5** geometry of CHF_3...HNO is slightly larger than in that of $CHCl_3$...HNO. This magnitude order of deprotonation enthalpy is directed to that of the intramolecular hyperconjugative energy resulting in transfer of electron density from nX to σ*(C4-H5) orbital. The calculated values of this work obtained at MP2/6-311++G(d,p) level of theory are in turn 27.33, 21.36 and 15.45 kcal.mol^{-1} going from CHF_3 to $CHCl_3$ to $CHBr_3$. It means that the larger the intramolecular hyperconjugative energy from nX to σ*(C4-H5) orbital is, the larger the deprotonation energy of C-H bond is. There is little sensitivity to identify the halogen atom because the difference of binding energies is small, *ca* 1.0 kJ.mol^{-1}, in each geometrical type upon going from F to Cl to Br.

Table 1: Interaction energies with BSSE ((ΔE(BSSE), in kJ.mol^{-1}) and both BSSE and ZPE ((ΔE(ZPE+BSSE), in kJ.mol^{-1}) corrections of complexes and the distances of hydrogen bond (R, in Å)

		S1	**S2**	**S3**	**S4**	**S5**
CHF_3-HNO	ΔE(BSSE)	-7.87	-7.19	-9.38	-8.28	-7.87
	ΔE(ZPE+BSSE)	-4.47	-3.47	-5.67	-5.35	-4.92
	R(H5...O1(N2))	2.60	2.67	2.62	2.72	2.45(2.57)[a]
	R(H3...X(6,7,8))	2.39	2.62	2.81	3.08	
	C4H5O1(N2)	120.2	99.4	119.3	100.8	164.2(136.1)[b]
	N2H3X(6,7,8)	129.3	118.7	90.6	81.0	
$CHCl_3$-HNO	ΔE(BSSE)	-7.90	-8.07	-9.79	-9.79	-7.70
	ΔE(ZPE+BSSE)	-4.43	-5.02	-6.57	-6.28	-4.12
	R(H5...O1(N2))	2.36	2.46	2.37	2.45	2.37(2.45)[a]
	R(H3...X(6,7,8))	2.86	3.06	3.41	3.39	
	C4H5O1(N2)	141.4	120.4	143.3	121.0	164.5(135.1)[b]
	N2H3X(6,7,8)	131.1	119.7	86.1	84.5	
$CHBr_3$-HNO	ΔE(BSSE)	-8.91	-9.03	-10.67	-10.97	-8.20
	ΔE(ZPE+BSSE)	-5.65	-6.35	-7.41	-7.72	-5.15
	R(H5...O1(N2))	2.34	2.45	2.33	2.41	2.34(2.47)[a]
	R(H3...X(6,7,8))	3.00	3.18	3.58	3.52	
	C4H5O1(N2)	146.1	125.4	148.7	126.1	168.6(139.2)[b]
	N2H3X(6,7,8)	132.8	121.1	86.3	85.4	

a refers to the H5...N2 distances; b refers to the C4H5N2 angle; the scaling factor for ZPE is 0.97.

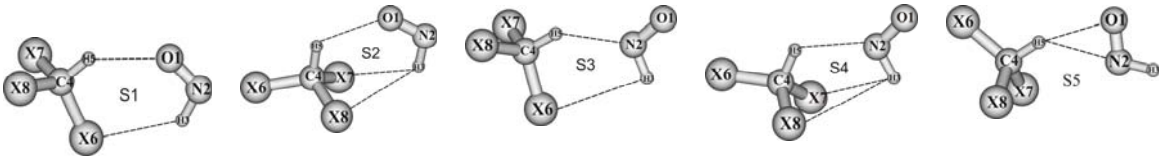

Figure 1: The geometries of optimized structures of the complexes pairing CHX_3 (X: F, Cl, Br) with HNO

Similarly, the H5...O1(N2) intermolecular distances tend to decrease, which is consistent with the increase of the polarity of the C-H bond. On the other hand, there is a increase of the H3...X(6,7,8) distances in going from F to Cl to Br, as shown in table 1. It should be explained that this order of increase depends on the size and NBO charge of X atom.

From the result of table 1, it indicates that the strength of the complex going from F to Cl to Br is determined by the distance of the H5...O1(N2) contact and the C4H5O1(N2) angle in each geometry. This is because the smaller the deviation of the angle from linearity is, the larger the overlap of electron density between the σ*(C4-H5) and n(O1) or n(N2) orbital is. This larger overlap leads to the complex becoming more stable. The change of bond lengths and stretching frequencies and infrared intensities of the C4-H5 and N2-H3 bonds is listed in table 2.

Table 2: The change of bond lengths of the C4-H5 and N2-H3 bonds (Å), their stretching frequencies (cm^{-1}) and infrared intensities ($km.mol^{-1}$) in the examined complexes compared to monomers respectively

		S1	**S2**	**S3**	**S4**	**S5**
CHF_3-HNO	Δr(C4-H5)	-0.0017	-0.0021	-0.0019	-0.0025	-0.0025
	Δr(N2-H3)	-0.0029	-0.0021	-0.0017	-0.0010	-0.0024
	Δν(C4-H5)	25.48	28.37	28.27	33.12	39.37
	Δν(N2-H3)	61.56	48.48	34.7	25.28	43.05
	ΔI(C4-H5)	-18.03	-16.12	-19.62	-13.61	-25.65
	ΔI(N2-H3)	-66.08	-57.88	-47.16	-42.04	-30.11
$CHCl_3$-HNO	Δr(C4-H5)	-0.0015	-0.0011	-0.0009	-0.0011	-0.0023
	Δr(N2-H3)	-0.0019	-0.0010	-0.0016	-0.0009	-0.0019
	Δν(C4-H5)	27.85	21.12	16.39	21.58	41.02
	Δν(N2-H3)	43.81	31.88	31.76	23.95	38.4
	ΔI(C4-H5)	12.66	3.49	33.80	10.17	16.31
	ΔI(N2-H3)	-63.38	-55.96	-54.99	-52.11	-18.80
$CHBr_3$-HNO	Δr(C4-H5)	-0.0012	-0.0009	-0.0004	-0.0008	-0.0019
	Δr(N2-H3)	-0.0017	-0.0011	-0.0016	-0.0011	-0.0018
	Δν(C4-H5)	22.51	17.51	7.44	15.13	35.62
	Δν(N2-H3)	39.41	30.98	32.11	26.12	36.08
	ΔI(C4-H5)	28.70	10.97	70.09	27.77	36.21
	ΔI(N2-H3)	-67.88	-58.87	-58.89	-57.33	-11.66

The Δr(C4-H5) and Δr(N2-H3) values are all negative, indicating that these hydrogen bonds are shortened upon complexation. Simultaneously, there is an increase of the respective C4-H5 and N2-H3 stretching frequencies. However, there is a different change of infrared intensity between the N2-H3 and C4-H5 bonds via complex formation. The decrease of the infrared intensity is observed in all the N2-H3 bonds and the C4-H5 bonds of the complexes of CHF_3 with HNO, corresponding to the increase of the respective stretching frequencies. Contrastly, there is an increase of the infrared intensities of the C4-H5 bonds in case of complexes between CHX_3(X = Cl, Br) and HNO. It should be explained that the different change of the infrared intensity depends on the nature of the CHX_3 isolated monomers. In particular, there is signal difference of dipole moment derivative along the C-H stretch of CHF_3, $CHCl_3$ and $CHBr_3$ [10]. Both the contraction of the C4-H5 and N2-H3 bonds and the increase of their stretching frequencies indicate that they are blue-shifting hydrogen bonds upon complexation. Such a contraction in the N-H covalent bond is extremely rare; this bond is normally elongated when a hydrogen bond is formed. The blue shift in the N2-H3 bonds is larger than in the C4-H5 bonds. It may be noted that the degree to which the C-H bond contracts is largest for X=F and least for X=Br. The inversely proportional linear correlations between the change of C4-H5 and N2-H3 bond lengths and their respective stretching frequencies are obtained as in equation (1) and (2), and plotted in figure 2.

$$\Delta\nu(\text{C-H}) = -14203\ \Delta r(\text{C-H}) + 4.6487 \quad (r = 0.959) \qquad (1)$$

$$\Delta\nu(\text{N-H}) = -16195\ \Delta r(\text{N-H}) + 9.8371 \quad (r = 0.929) \qquad (2)$$

It is interesting that the N2-H3 bonds are significantly contracted in the **S5** geometries although they don't participate in hydrogen bond. It indicates that the contraction of N2-H3 bond corresponding to an increase of its stretching frequency depends on nature of the isolated HNO monomer. This new direction has been recently studied and will be continued in our following papers. Along with the contraction of the C4-H5 and N2-H3 bonds in each geometrical structure, there is a change of bond length of the remaining bonds. Particularly, all N2=O1 bonds are lengthened when the complexes are formed. Besides, the hydrogen bonded C-X bonds are elongated and the hydrogen non-bonded C-X bonds are contracted upon complexation, except for the elongation of all the C-X bonds in the **S5** geometries going from F to Cl to Br.

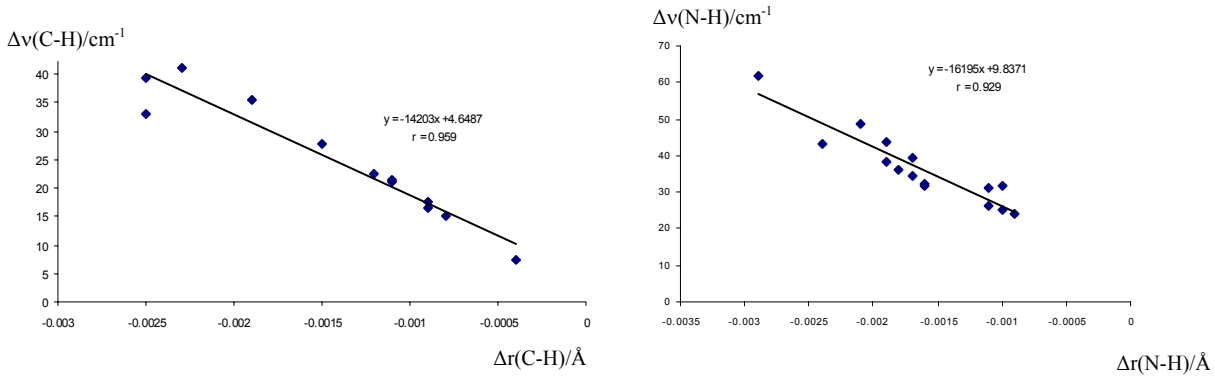

Figure 2: The linear correlation between the change of the stretching frequencies and that of the bond length

2. NBO analysis

To get more information on the blue shifts of the C4-H5 and N2-H3 stretching frequencies, NBO analysis has been carried out at the MP2/6-311++G(d,p) level. The corresponding results are reported in table 3.

Table 3: NBO analysis and R_E energy index

		S1	S2	S3	S4	S5
CHF_3-HNO	EDT/e	0.0009	0.0010	0.0025	0.0014	0.0045
	Δσ*(C4-H5)/e	-0.0012	-0.0015	-0.0004	-0.0010	-0.0005
	Δσ*(N2-H3)/e	-0.0016	-0.0011	-0.0005	-0.0003	-0.0013
	Δ%s(C4-H5)	0.48	0.48	0.57	0.50	0.69
	Δ%s(N2-H3)	0.54	0.41	0.53	0.45	0.60
	R_E(C4-H5)	0.51	0.18	0.75	0.33	0.77(0.26)[c]
	R_E (N2-H3)	0.42	0.29	0.00	0.00	0.00
$CHCl_3$-HNO	EDT/e	0.0007	0.0003	0.0044	0.0008	0.0051
	Δσ*(C4-H5)/e	-0.0023	-0.0017	-0.0012	-0.0014	-0.0020
	Δσ*(N2-H3)/e	-0.0007	-0.0005	-0.0002	-0.0000	-0.0011
	Δ%s(C4-H5)	0.86	0.62	1.16	0.84	0.99
	Δ%s(N2-H3)	0.48	0.40	0.57	0.50	0.55
	R_E(C4-H5)	0.70	0.41	0.89	0.53	0.69(0.15)[c]
	R_E (N2-H3)	0.65	0.42	0.00	0.00	0.00
$CHBr_3$-HNO	EDT/e	0.0005	0.0003	0.00552	0.0012	0.0057
	Δσ*(C4-H5)/e	-0.0020	-0.0013	-0.00075	-0.0010	-0.0018
	Δσ*(N2-H3)/e	-0.0003	-0.0003	-0.00016	-0.0001	-0.0012
	Δ%s(C4-H5)	1.02	0.69	1.45	1.00	1.15
	Δ%s(N2-H3)	0.51	0.44	0.57	0.53	0.51
	R_E(C4-H5)	0.87	0.53	1.07	0.69	0.85(0.13)[c]
	R_E (N2-H3)	0.80	0.53	0.00	0.00	0.00

[c]refers to the energy index for interaction transferring electron from the N2 to σ*(C4-H5) orbital.

EDT values are all positive, it means that there is electron density transfer from HNO to CHX_3 when the complex is formed. As shown in table 3, the electron density decrease in both the σ*(C4-H5) and σ*(N2-H3) anti-bonding orbitals. The decrease of the electron density in the σ*(C4-H5) and σ*(N2-H3) orbitals strengthens the C4-H5 and N2-H3 bonds, which contributes to the blue shift of the corresponding stretching frequency. Simultaneously, the increase in s-character of the C4 and N2 hybrid orbitals in the C4-H5 and N2-H3 bonds is also observed in all the examined complexes. As a result, this increase strengthens the C4-H5 and N2-H3 bonds and results in the contraction of these bonds corresponding to increase in their stretching frequencies. In a word, the contraction of the C4-H5 and N2-H3 bonds corresponding to the blue shift of stretching frequencies is contributed by both the increase of s-character and the decrease of electron density in the σ-antibonding orbital.

The variation of the occupation of σ-antibonding orbitals results from two effects acting in opposite directions. If we consider a Z-X-H...Y hydrogen bond, the intermolecular n(Y)

to σ*(XH) hyperconjugative interaction leads to an increase in electron density in the σ*(XH) orbital. In contrast, a decrease of the n(Z) → σ*(XH) intramolecular interaction with respect to the monomer, has the opposite effect and results in a decrease in occupation of the σ*(XH) orbital. On the basis of these considerations, it may be useful to use the R_E index defined as follows [10, 11].

$$R_E = \frac{E^{(2)}_{inter}}{E^{(2)}_{intra}}$$

where $E^{(2)}_{inter} = E^{(2)}[n(Y) \rightarrow \sigma^*(XH)]$

$$\Delta E^{(2)}_{intra} = E^{(2)}_{mon}[n(Z) \rightarrow \sigma^*(XH)] - E^{(2)}_{compl}[n(Z) \rightarrow \sigma^*(XH)]$$

The R_E values of the C4-H5 bonds are from 0.00 to 1.16, while that of the N2-H3 bonds from 0.00 to 0.80. All these R_E values are smaller than 2.98 which is upper limited value of R_E for the blue shift of the C-H bonds in ref 10 and 11. Therefore, the R_E index can be used to consider the classification of blue-shifting or red-shifting hydrogen bond. The R_E index with the zero value indicates that for the **S3**, **S4** and **S5** geometries going F to Cl to Br, there is no transfer of the electron density from the n(X) to σ*(N2-H3) orbital as shown in Table 3. Hence, the decrease in electron density of the σ*(N2-H3) orbital results from the decrease in the intramolecular n(O1) to σ*(N2-H3) hyperconjugative interaction. The dual correlation between the change of the N2-H3 bond lengths, that of the electron density in the σ*(N2-H3) orbitals, and that of hybridization in the N2 hybrid orbitals when the **S5** geometries are obtained as the following:

$$\Delta r(N\text{-}H) = 1.174967\Delta\sigma^*(N\text{-}H) - 0.00438\Delta\%s(N\text{-}H) + 0.001176 \quad (r = 0.962) \quad (3)$$

$$\Delta\nu(N\text{-}H) = -23017.68905\Delta\sigma^*(N\text{-}H) + 33.134337\Delta\%s(N\text{-}H) + 8.471835 \quad (r = 0.959) \quad (4)$$

To check of reliability of these correlations, we calculated the change of the bond length and the stretching frequency based on equation (3) and (4). The results indicate that the correlations are reasonable and reliable as follows:

$$\Delta r(N\text{-}H)_{calculation} = 0.9256\ \Delta r(N\text{-}H)_{theoretical} - 0.0001 \quad (r = 0.962) \quad (5)$$

$$\Delta\nu(N\text{-}H)_{calculation} = 0.9189\ \Delta\nu(N\text{-}H)_{theoretical} + 2.9064 \quad (r = 0.959) \quad (6)$$

IV - CONCLUDING REMARKS

Each complex pairing HNO and CHX_3 (X: F, Cl, Br) contains five separate minima on the potential energy surface. The binding energies obtained at the MP2/6-311++G(d,p) level are from 7 to 11 $kJ.mol^{-1}$ with the BSSE correction and from 4 to 8 $kJ.mol^{-1}$ with both the ZPE and BSSE corrections. The most stable are the complexes pairing $CHBr_3$ with HNO, and the least stable are the complexes between CHF_3 and HNO. The difference is due to the deprotonation enthalpy of the C-H bond which is the smallest in the $CHBr_3$ and the largest in the CHF_3. The contractions of the bond length and the blue shifts of the stretching frequency are observed in all the N2-H3 and C4-H5 bonds going from F to Cl to Br. However, the infrared intensities of the C4-H5 bonds are increase in the complexes of $CHCl_3$...HNO and $CHBr_3$...HNO, while the decrease of the infrared intensities is obtained in the complexes of CHF_3...HNO. The shortening of the C-H bond and blue shift of its stretching frequency depend on the nature of the proton donor, particularly the polarity of the C-H bond. The EDT and R_E can be used for classification of type of hydrogen bond.

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REFERENCES

1. G. R. Desiraju; T. Steiner. The Weak Hydrogen Bond in Structural Chemistry and Biology, Oxford University Press, New York (1999).
2. Grabowski, S. J. Ed. Hydrogen Bonding-New Insights, Springer, Dordrecht, the Netherlands (2006).
3. Y. Yang, W. J. Zhang, X. M. Gao. Int. J. Quant. Chem., **106**, 1199 (2006).

4. Y. Liu, W. Liu, H. Li, J. Liu, J. Yang. J. Phys. Chem A, **110**, 11760, (2006).
5. M. Solimannejad, S. Scheiner. J. Phys. Chem. A, **111**, 4431 (2007).
6. M. J. Frisch and et al., Gaussian 03, Revision B.03, Gaussian Inc., Pittsburgh, PA (2003).
7. S. F. Boys, F. Bernardi. Mol. Phys., **19**, 553 (1970).
8. A. E. Reed, L. A. Curtiss, F. Weinhold. Chem. Rev., **88**, 899 (1988).
9. J. E. Bartmess, J. A. Scott, R. T. McIver. J. Am. Chem. Soc., **101**, 6047, (1979); J. A. Paulino, R. R. Squires. J. Am. Chem. Soc., **113**, 5573 (1991); M. Born, S. Ingemann, N. M. Nibbering. Int. J. Mass Spectrom., **194**, 103 (2000).
10. Nguyen Tien Trung, Tran Thanh Hue. Journal of Chemistry, **45**, 685 (2007).
11. Nguyen Tien Trung, Nguyen Phi Hung, Tran Thanh Hue, Journal of Chemistry, **46**, 7 (2008).